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Radiolysis of Solid Inorganic Salts with Oxygen-containing Anions

Yu.A.Zakharov and V.A.Nevostruev

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I. INTRODUCTION

The extent and rate at which investigations have been made in the field of the radiation chemistry of solid inorganic compounds has been continuously increasing in recent years. The amount of information accumulated in the specialist literature on these problems is now very large. Data published up to 1962 were reviewed systematically by Sviridov[1], but there are no later reviews.

The aim of the present review was to arrange systematically and to discuss data on the radiation-induced reactions in the group of salts investigated in the greatest detail—alkali metal nitrates, nitrites, chlorates, bromates, and perchlorates. Particular attention has been devoted to the most recent investigations and the views formulated on their basis. Data published up to the end of 1966 are included in the review.

II. RADIOLYSIS OF NITRATES

Of all the inorganic salts with oxygen-containing anions, the nitrates have been investigated most vigorously, the study of alkali metal nitrates being the most detailed[2-11] and that of the nitrates of silver[2,12], alkaline earth metals[2,13,14], and lead[2,15-17] less so.

1. Products of Radiolysis

a. Optical spectra of irradiated nitrates. One of the first studies on optical absorption by irradiated sodium nitrate was that by Pringsheim[18]. At the temperature of liquid nitrogen an absorption band with a maximum at 335 nm was observed and at room temperature another band with a maximum at 355 nm appeared in addition. The author attributed the first band to an electron-excess centre and the second to NO_2^- ions. Absorption maxima at about 350 nm were also observed by Johnson[17] in the reflection spectra of irradiated potassium and lead nitrates. Cunningham made the most detailed study of this problem in the case of potassium nitrate[4]. Fig. 1, which is taken from his paper, shows the absorption spectrum of a potassium nitrate crystal irradiated at 4.2°K. In the range of doses less than 10^{20} eV g^{-1} six absorption bands were observed both at 4.2°K and at 77°K with maxima at 520, 355, 325, 290, 268, and 250 nm. The study of the behaviour of these bands on irradiation with light at a definite wavelength and on changing the temperature, and also comparison with the behaviour of ESR signals on treatment of this kind enabled the author[3,4] to identify these absorption bands. Thus the absorption at 250 nm was

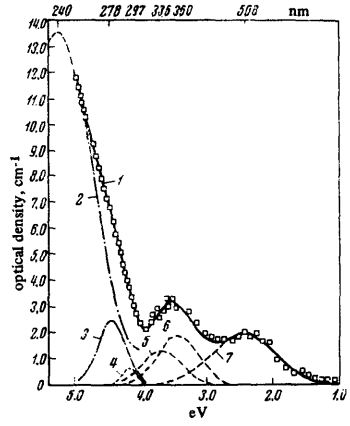


Figure 1. Optical absorption spectrum of potassium nitrate irradiated with γ-rays at 4.2°K;[4] the symbols denote experimental values; curve *1* was obtained by adding together curves *2–7*.

attributed to NO_3 radicals, that at 268 and 520 nm to NO_2^{2-} radical-ions, and that at 325 nm to NO_3^{2-}.

The centre responsible for the band at 290 nm, which is stable at the temperatures of liquid helium and liquid nitrogen, but is annealed on heating to room temperature, was not identified. Nor was the absorption band at 355 nm, which Pringsheim[18] attributed to nitrite ions, assigned.

However in a later study [19] Cunningham assigned this absorption band (*C*-centre) to the oxyhyponitrite ion $N_2O_3^{2-}$.

On irradiation of potassium nitrate with a dose in excess of 10^{20} eV g^{-1}, an additional absorption band was observed at 410 nm. Like the ESR signal [3] attributed to NO_2, which also appears at doses greater than 10^{20} eV g^{-1}, this absorption band was assigned to NO_2.

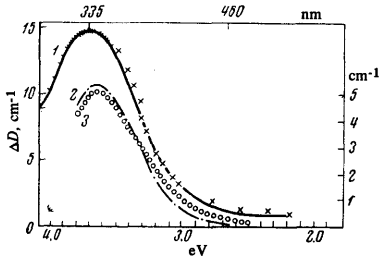


Figure 2. Light absorption by sodium nitrate [19]: *1*) irradiation with X-rays at 77°K for 75 min (right-hand scale); *2*) irradiation with γ-rays at 77°K for 30 min (left-hand scale); *3*) as for 2 after irradiation with $\lambda > 510$ nm light at 77°K for 40 min.

The spectrum of sodium nitrate [19] irradiated at 77°K was found to contain one absorption band with a maximum at 335 nm (Fig. 2). However, analysis of the shape of the curve and experiments involving bleaching with ultraviolet light enabled the author to identify two species responsible for this band (NO_2^{2-} and NO_3^{2-}) and to detect absorption at 410 nm, which is attributed to NO_2. It is interesting that

Table 1. Optical centres in irradiated nitrate systems.

Postulated absorption centre	λ_{max}, nm	Matrix	*T*, °K	Refs	Remarks
NO_3	250	KNO_3	4.2and77	4	Pulse radiolysis
NO_3	600,640,670	$H_2O + NaNO_3$	300	20	
NO_2	598,635,671	$Ce(NO_3)_4 + 6MHNO_3$		20	Flash photolysis
NO_3^{2-}	325	KNO_3	4.2and77	4	
NO_3^{2-}	335	$NaNO_3$	77	19	
NO_2	410	KNO_3	4.2and77	4	
NO_2	410	$NaNO_3$	77	19	
NO_2	400			20	
NO_2^{2-}	268,520	KNO_3	4.2and77	4	
NO_2^{2-}	335	$NaNO_3$	77	19	
NO_2^-	355	$NaNO_3$	300	18	
$N_2O_3^{2-}$	355	KNO_3	77	19	Stable up to 300°
NO_2^-	~350	KNO_3 and $Pb(NO_3)_2$	300	17	Reflection spectrum
$\bar{e}_{stab}$	335—340	$NaNO_3$	77and300	18	

Cunningham [19] observed an inhibiting effect by Ag^+ ions, introduced into the potassium nitrate and sodium nitrate lattices, on the increase in the intensity of the absorption bands assigned to nitrate ion conversion products.

Table 1 lists the optical centres in irradiated nitrates. For comparison, data obtained on the irradiation of liquid solutions of nitrates are included.

b. ESR Spectra of irradiated nitrates. The ESR signals in irradiated nitrates of potassium [3,5,7,21,22] and sodium [23-28] have been investigated in relatively great detail. There is also information about the ESR spectra of irradiated nitrates of silver [12] strontium [13,29], lead [16,29], and barium [29]. All the nitrates investigated were found to contain NO_2. NO_3 radicals were detected in potassium nitrate [3,5], sodium nitrate [25], and lead nitrate [16], and NO_3^{2-} species were found in potassium nitrate [3,5,21,24], lead nitrate [29], barium nitrate [29], strontium nitrate [13,29], and silver nitrate [12]. In the nitrates of silver [12], lead [29], and, to a slight extent, barium [29] the signal due to the unpaired electron is also split by the cations, i.e. in these nitrates the entire molecule and not only the anion serves as the electron trap. Therefore, especially in silver nitrate, the paramagnetic molecule $(AgNO_3)^-$ appears instead of NO_3^{2-}.

Table 2. Characteristics of the ESR spectra of the paramagnetic species in irradiated potassium nitrate single crystals

Postulated radical	*g*-Factor			Hyperfine structure constants, G			References	Remarks
	g_x	g_y	g_z	A_z	A_x	A_y		
1	2			3			4	5
NO	2.008	2.010	2.005	3.5	4.0	31	3	77° and 4°K
NO_2	1.9996	1.9932	2.0055	62.9	50.3	48.7	21	Formed on heating to room temperature between two exposures to radiation at 77°K or in the presence of potassium nitrite
NO_3		1.999			113		3	Potassium nitrate powder, dose 3×10^{20} eV g^{-1}
NO_3^{2-}	2.025	2.025	2.008	9	9	9	3	4°K, dose 3×10^{18} eV g^{-1}. Absent at 77°K; on annealing at 77°K for 2 h decreases by a factor of two
NO_3^{2-}	2.0057	2.0057	2.0015	63.4	31.8	31.8	5	77°K, dose 4×10^{19} eV g^{-1}, *H* parallel to *a*
NO_2^{2-}	2.006	2.006	2.002	61	32	32	3	4° and 77°K. Crystal axis *c* parallel to rotation axis and perpendicular to *H*
NO_3	2.006	2.006	2.001	0	0	0	3	4°K
NO_3	2.0232	2.0232	2.0031	4.3	3.5	3.5	5	77°K, rapidly decomposes at this temperature
O_2^-		1.958			0		3	Singlet. Appears on heating to 77°K or in measurements at 4°K on a crystal irradiated at 77°K

Furthermore, in silver nitrate there is also an ESR signal due to Ag^{2+} ions [12], the characteristics of which are not given in Table 4. The presence of NO, NO_2^{2-}, and O_2^- in irradiated potassium nitrate has been indicated only by Cunningham [3]. Thus different workers have identified different paramagnetic species in the same nitrate (potassium nitrate) and under the same or similar conditions. These discrepancies are illustrated by the characteristics of the spectra attributed to the paramagnetic species in irradiated potassium nitrate (listed in Table 2).

Although the ESR spectra of irradiated sodium nitrate have been studied in a number of investigations [23-28], only the spectrum attributed to nitrogen dioxide has been reliably interpreted. In two studies [25,28] NO_3 radicals have been identified in addition to NO_2. Table 3, which lists the characteristics of the ESR signals in sodium nitrate, shows that different spectra are attributed to NO_3 radicals. It has been shown [26] that the matrix has virtually no influence on the characteristics of the ESR spectrum due to NO_2. Therefore there is no doubt about the presence of NO_2 in other nitrates also, as can be seen from Tables 2–4. Certain contradictions in the identification of the individual paramagnetic species are readily seen from a comparison of the data in Tables 2–4.

1. If the spectroscopic characteristics of particular paramagnetic species remain the same or similar in the lattices of different nitrates (which probably in fact is the case), the ESR spectrum attributed to NO_2^{2-} in potassium nitrate by Cunningham[3], to NO_3^{2-} in potassium nitrate by Zeldes[22], to NO_3^{2-} in silver nitrate by Mosley and Moulton[12], and to NO_3^{2-} in potassium chloride containing nitrate by Jaccard[30] should be assigned to one of these paramagnetic species. This also applies to the interpretation of the spectra attributed to NO_3^{2-} in potassium nitrate by Cunningham[3] and in strontium nitrate by Zdansky and Sroubek[13] and to NO_3 species in potassium nitrate by Livingston and Zeldes[5] and in lead nitrate by Golding and Henchman[16]. This problem was examined in fair detail by Atkins and Symons[31]. On the basis of a comparison of the characteristics of these spectra with those of isoelectronic radicals, they assigned the first spectrum with $g_x = g_y = 2.006$, $g_z = 2.002$, $A_x = A_y = 32$–37 G, and $A_z = 61$–68 G to NO_3^{2-} radicals, and the second, with very slight splitting, to NO_3.

Table 3. Characteristics of the ESR spectra of sodium nitrate.

Irradiation temperature, °K	Paramagnetic species	$g_{\parallel}$ <111>	$g_{\perp}$ <111>	$A_{\parallel}$ <111>	$A_{\perp}$ <111>	References	Remarks
300	NO_2	2.0059	1.9982	48.0	58.4	24	
77	NO_2	2.0058	1.9964	50.5	59.1	26	
170	NO_2	2.0056	1.9966	51.1	58.4	27	
300	NO_2	2.0050	1.9970	53.0	57.8	27	
300	NO_2	2.006	1.9989	53	59	25	Disappears at 400°K
300	?	2.006	2.0097	0	0	25	ditto
300	?	2.0064	2.0147	0	0	25	Stable above 530°K
300	?	2.006	2.0237	0	0	25	Disappears at 400°K
77	NO_3	2.0004	2.0053	0	0	25	At 300°K converted irreversibly into three preceding species
77	NO_3	2.0022	2.0217	4.11	3.51	28	
77	?	2.0030	2.0225	0	0	28	

2. The spectrum which Cunningham[3] and Jaccard[30] attributed to NO radicals is assigned by Atkins and Symons[31] to NO_2^{2-} species. However, Cunningham[7] showed by chemical analysis and by the ESR method that NO species accumulate as the dose is increased. The two methods gave satisfactory agreement. The data are presented in Fig. 3. Because of this, and also in consequence of the very high anisotropy of the hyperfine splitting, Cunningham's view on this problem is probably more correct.

The identification of the radicals NO_3, NO_3^{2-}, and NO_2^{2-} requires additional investigations.

c. Composition of stable products. The generally adopted method for the determination of the final radiolysis products of nitrates involves the determination of the nitrite by diazotisation after dissolution of the irradiated nitrate in water. In the vast majority of cases the solutions of irradiated nitrates were analysed for nitrite only. In those studies where the gases evolved from the solution were analysed (see, for example, Refs. 2, 7, 19), it was shown that the gaseous radiolysis product is oxygen. The ratio $G(NO_2^-):G(O_2) \simeq 2$ is maintained in all cases, except for the initial stage in the radiolysis of lead nitrate[17].

However, it should be noted that there is a possibility of chemical reactions of the radiolysis products on dissolution of irradiated nitrate in water. Cunningham[7] showed that radical products such as O^-, NO_2, and NO may make a contribution to the yields of the radiolysis product determined as nitrite by the diazotisation reaction. On dissolution in water these products alter the concentration of nitrous acid by the following reactions:

$$O^- + H_2O \rightarrow OH + OH^-,$$
$$OH + NO_2^- \rightarrow NO_2 + OH^-,$$
$$2NO + O_2 \rightarrow 2NO_2,$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2.$$

Table 4. Characteristics of the ESR spectra of irradiated non-alkali metal nitrates.

Paramagnetic species	irradiated salt	g-Factor			Hyperfine structure constants, G			Refs	Remarks
		g_x	g_y	g_z	A_x	A_y	A_z		
NO_2	$AgNO_3$	2.009	1.9978	2.0039	50.7	48.5	69.6	12	Irradiation at 77°K. Intensity increases with disappearance of the Ag^{2+} signal on heating the crystal from 77° to 140°K
NO_2	$Sr(NO_3)_2$	1.9975	1.9975	2.0054	59	59	50	13	Room temperature. Formed at about 10^7 r or at about 10^5 r if the nitrate contains nitrite
NO_2	$Pb(NO_3)_2$	1.995	1.995	2.004	57	57	50	16	Room temperature
NO_3	$Pb(NO_3)_2$	2.029	2.029	1.998	1	1	2	16	ditto
NO_3^{2-}	$AgNO_3$	2.002	2.007	2.000	35.8	37.1	67.4	12	77°K. The unpaired electron is not localised at NO_3^-, but there is a hyperfine structure also due to the nucleus of the neighbouring cation
NO_3^{2-}	$Sr(NO_3)_2$	2.0081	2.0081	2.0027	0	0	0	13	Room temperature
NO_3^{2-}	$Sr(NO_3)_2$	2.0019	2.0060		68.8	37.3		29	90°K
NO_3^{2-}	$Pb(NO_3)_2$	1.9857	1.9912		66	36.5		29	
NO_3^{2-}	$Ba(NO_3)_2$	1.9997	2.0053		66.3	34.7		29	

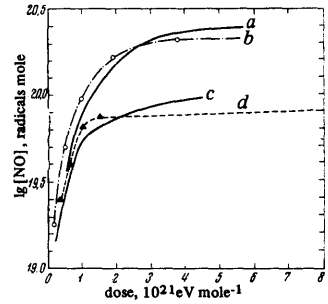


Figure 3. Formation of NO in potassium and sodium nitrates irradiated at 77°K:
a) and *c*) curves based on chemical analysis; *b*) and *d*) curves obtained by the ESR method[7].

It follows from this that $G(NO_2^-)$ determined by the diazotisation method includes the yields of other products: $G(NO_2^-) = G(NO_2^-)_{true} + \frac{1}{2}G(NO_2) + \frac{1}{2}G(NO) - \frac{1}{2}G(O^-)$. It can probably be regarded as established that the main radiolysis products at room temperature, at any rate for potassium and sodium nitrates, are NO, NO_2^-, NO_2, and oxygen. As shown by Cunningham[7], the presence of nitrogen in the gaseous radiolysis products noted by Hennig et al.[11] is a result of the desorption of air adsorbed on the surface of the nitrates during irradiation.

2. Kinetics of Radiolysis

Since nitrogen-containing radiolysis products of nitrates were determined by the diazotisation method in all the investigations except that of Cunningham[7], and since there are no data in the literature on the accumulation of all the decomposition products of NO_3^-, we shall henceforth examine the kinetics of the radiolysis of nitrates on the basis of the yield of nitrite, but one must remember that $G(NO_2^-)$ includes several components (see above).

a. Dependence of the radiochemical yield on the dose absorbed. This problem was investigated in greatest detail by Johnson and coworkers[2,32]. Using the decomposition mechanism for the nitrates of potassium, caesium, sodium, barium, lead, and silver,

$$MNO_3 \xrightarrow{h\nu} MNO_2 + O \quad , \tag{1}$$

$$O + NO_2^- \rightarrow NO_3^- \quad , \tag{2}$$

$$O + NO_3^- \rightarrow NO_2^- + O_2 \quad , \tag{3}$$

and applying the method of steady-state concentrations to atomic oxygen, they derived a second-order equation for the accumulation of nitrite:

$$a[NO_2^-]^2 + [NO_2^-] = bD \quad , \tag{4}$$

where a and b are constants for the given salt and D is the dose absorbed. Eqn. (4) describes satisfactorily the experimental data for caesium, sodium, barium, and lead nitrates (Fig. 4).

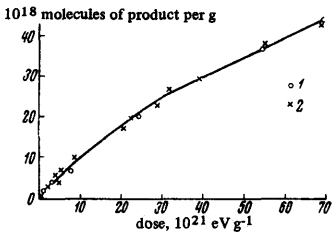


Figure 4. Formation of nitrite[2] in sodium nitrate: *1*) $[NO_2^-]$; *2*) $\frac{1}{2}[O_2]$; curve calculated from Eqn.(4).

From the above mechanism of radiolysis [Eqns. (1)–(3)], the following equation for the description of the accumulation of nitrite in potassium nitrate was obtained taking into account the changes in the concentration of NO_3^- ions[2]:

$$a \lg(1-\alpha) + \frac{\alpha}{1-\alpha} = bD \tag{5}$$

(where $\alpha = [NO_2^-]/[NO_3^-]_0$, a and b are constants, and D is the dose absorbed).

Cunningham and Heal[33], who used doses in excess of 10^{33} eV g^{-1}, described the kinetics of the radiolysis of potassium nitrate by the equation

$$\alpha = 1 - e^{bD} \tag{6}$$

where α is the fraction of nitrate decomposed, D the dose absorbed, and b a constant. A suitable equation for the kinetics of the radiolysis of silver nitrate could not be derived from the decomposition mechanism based on reactions (1)–(3).

The independence of $G(NO_2^-)$ of the dose for the individual nitrates, noted in numerous studies[1,8,10,17,34-36], is observed only for low doses, which are different for different nitrates. It is not difficult to see that all three kinetic equations [Eqns. (4)–(6)] degenerate at low doses to an expression of the form

$$[NO_2^-] = bD \quad , \tag{7}$$

which is consistent with the initial linear sections of the NO_2^- ion accumulation curves.

b. Effect of dose rate and LET†. The effect of dose rate on the radiolysis of nitrates has been investigated in numerous studies[10,33,35,37]. $G(NO_2^-)$ for the nitrates of potassium, sodium, caesium, and lead[37] was not found to change on varying the dose rate from 10^{17} to 10^{20} eV g^{-1} s^{-1}, as observed in other investigations[10,33,35] in the region of other dose rates and for other forms of radiation. The independence of the yield of nitrite of dose rate over a wide range (from about 10^{15} to 10^{20} eV g^{-1} s^{-1}) permitted an unambiguous interpretation of the results on the effect of the type of radiation on $G(NO_2^-)$. Table 5, taken from Hochanadel's paper[10], lists the values of $G(NO_2^-)$ obtained in the radiolysis of nitrates by different types of radiation. The similarity of the values of $G(NO_2^-)$ obtained

Table 5. Effect of LET on $G(NO_2^-)$ in nitrates[10].

Irradiated salt	3.4 MeV α-particles		^{60}Co γ-rays		44.5 keV X-rays	
	25°	120°	30°	150°	15°	150°
$LiNO_3$	0.7		0.02—0.2	0.03—0.4	0.02	
$NaNO_3$	1.3	1.1	0.27	1.0	0.4	1.1
KNO_3	2.2		1.5	3.0	2.0	3.0
$CsNO_3$	1.4		1.6	2.3	1.4	1.2
$Ba(NO_3)_2$	1.6		1.8	1.6	1.8	1.8

under the action of X-rays and γ-rays at 150°C and those obtained under the action of α-rays at 25°C led the author to the conclusion that thermal spikes are formed in the tracks of α-particles. The increase of the radiochemical yield of nitrite with increase in LET was attributed to a local temperature rise in the tracks of heavy particles. It should be noted, however, that it has been demonstrated quite recently that thermal spikes are not formed in the radiolysis of certain salts by protons[38].

c. The role of the cation. Even in the first studies on this problem, a definite relation between $G(NO_2^-)$ and the nature of the cation in nitrates was noted. The present generally accepted explanation is derived by considering the effect of the free space of the lattice on the probability of the reverse reactions. This problem is discussed in greater detail below.

d. Effect of other factors. The values of $G(NO_2^-)$ obtained by different workers show very appreciable discrepancies[1]. One of the possible reasons for the differences may be the different degrees of dispersion of

† Linear energy transfer (Ed.of Translation).

the nitrates irradiated[2,8]. The size of the crystals irradiated has a direct effect on the retention of gaseous radiolysis products within the lattice. On the other hand, the amount of gases retained influences the rate of the reverse reactions of the radiolysis products (see Section VI).

The influence of hetero-phase semiconductor oxide impurities[8] on the rate of radiolysis of potassium nitrate and sodium nitrate has also been investigated. Since the change in the rate of radiolysis under the influence of the oxides is correlated with the electron work functions of the latter, the effect of the additives on radiolysis was attributed to their donor-acceptor properties in relation to the nitrates. The decrease of the rate of radiolysis of sodium nitrate in the presence of Ag^+ ions in the sodium nitrate lattice was also attributed by Cunningham[19,34] to the acceptor properties of Ag^+. Accordingly, the introduction of Tl^+ ions, which, as shown by Boldyrev et al.[39] are electron donors, accelerates the radiolysis of potassium nitrate. Although the amount of experimental data is as yet insufficient to arrive at unambiguous conclusions concerning the mechanism of the effect of the admixtures, one may conclude that, like the degree of dispersion of the crystals, the purity of the salt irradiated has a significant influence on radiochemical stability.

3. Mechanism of Radiolysis

Although the nitrite ion accumulation curves are described satisfactorily by the kinetic equations based on reactions (1)–(3), the work of Cunningham[4,7,19,34] and the ESR spectroscopic data for irradiated nitrates, examined above, convincingly demonstrate a significantly greater complexity of both the primary and the secondary radiochemical processes in the irradiation of nitrates.

The primary processes must be regarded as ionisation and excitation processes:

$$NO_3^- \xrightarrow{h\nu} NO_3^-{}^*, \quad NO_3, \bar{e} \qquad (8a)$$

$$M^+ \xrightarrow{h\nu} M^{2+} + \bar{e} \qquad (8b‡)$$

We may note that NO_3 can probably form not only as a result of reaction (8a) but also in the subsequent reaction

$$M^{2+} + NO_3^- \rightarrow (M^+{}^* + NO_3) \rightarrow M^+ + NO + O_2 , \qquad (9)$$

which is confirmed by the effect of the nature of the cation on the yield, noted above. Because of the high degree of excitation of the cation, reaction (9) probably does not stop at the stage where NO_3 is formed and continues to a more profound decomposition of the anion. The NO_3 radicals formed in reaction (8a) are unstable even at 77°K (at room temperature the presence of NO_3 is suggested only for lead nitrate[16]) and can decompose by the reactions

$$NO_3 \rightarrow NO_2 + O , \qquad (10a)$$

$$NO_3 \rightarrow NO + O_2 , \qquad (10b)$$

or can serve as traps for thermalised electrons:

$$NO_3 + \bar{e} \rightarrow NO_3^-{}^* \rightleftarrows NO_2^- + O . \qquad (11)$$

Since the steady-state concentrations of NO_3 and thermalised electrons are insignificant, one may assume that reaction (11) is unlikely. Cunningham[3,7] found that NO is the primary product and NO_2 appears only for high values of the absorbed dose. It has also been stated in other papers[21,22] that NO_2 is a secondary product. Therefore reactions (10a) and (11) are unlikely, in contrast to reaction (10b). Since the electron affinity of NO_3 is greater than the energy of the N–O bond[40], the oxygen atom produced by fragmentation should have an excess kinetic energy of about 0.2 eV, if it is assumed that the energy associated with the electron affinity of the NO_3 radical is localised at a definite bond. On the other hand, in a solid the cage effect should be shown to the greatest extent. For these reasons, the excitation energy of $NO_3^-{}^*$ is often scattered by the crystal lattice and part of the $NO_3^-{}^*$ species break down into nitrite and atomic oxygen.

The secondary electron, thermalised in non-elastic collisions, may be stabilised in a trap of any type. Such traps may be the defects initially present in the lattice, ionisation products of the cation or anion, radiolysis products produced in secondary (see below) processes (O, O_2, NO_2, etc.), and finally normal lattice sites. In the last case it is reasonable to expect that in alkali metal and alkaline earth metal nitrates thermalised electrons are stabilised by anions and not cations, since the N^{5+}/N^{4+} redox potential is much higher than for M^+/M. Consequently the second primary product, in addition to NO_3, is electron-stabilised by anions[3–5,12,13,19,21,25,29]:

$$NO_3^- + \bar{e} \rightarrow NO_3^{2-} , \qquad (12)$$

but in silver nitrate, where the cation is an effective electron acceptor, we have $AgNO_3 + \bar{e} \rightarrow [Ag(NO_3)]^-$.

In potassium and sodium nitrates the absorption band and the ESR spectrum attributed to NO_3^{2-} vanish completely on heating the irradiated crystals to 300°K. At this temperature only the optical absorption bands attributed to $N_2O_3^{2-}$ and NO_2 are stable[4,19]. Consequently, apart from NO_3 radicals, species with an excess of electrons should make a contribution to the formation of the final radiolysis products:

$$NO_3^{2-} \rightarrow NO_2^- + O^- , \qquad (13)$$

$$NO_3^{2-} \rightarrow NO_2^{2-} + O . \qquad (14)$$

It is so far difficult to estimate the relative contributions to the yields of final radiolysis products by reactions (8)–(11) and (12)–(14). It is extremely probable that these two groups of reactions lead to different results. As already mentioned above, the relative importance of the individual reactions within each group is also different.

The present authors believe that steric factors should have a considerable effect on secondary processes involving the interaction of the products of reactions (8)–(14). Fig. 3 shows that the concentration of NO in sodium nitrate reaches a limiting value at a dose of only 1×10^{21} eV $mole^{-1}$, while in potassium nitrate the corresponding dose is approximately twice as high, the steady-state concentration of NO in sodium nitrate also being lower than in potassium nitrate. This shows that the reactions of NO depend on the lattice parameters. According to Cunningham, such reactions may be

$$NO + O \rightarrow NO_2 , \qquad (15)$$

$$NO + O_2^- \rightleftarrows NO_3^-{}^* \rightleftarrows NO_2^- + O , \qquad (16)$$

$$NO + NO_3 \rightleftarrows N_2O_4^* \rightleftarrows 2\,NO_2 , \qquad (17)$$

$$NO + NO_2^{2-} \rightarrow N_2O_3^{2-} , \qquad (18)$$

$$O + O = O_2 . \qquad (19)$$

Reaction (17) occurs only in the presence of high doses, when there is a possibility of the formation of NO and NO_3 at adjacent sites[7].

‡ Here and henceforth M^+ denotes the normal cation (Na^+, K^+, Sr^{2+}, Ba^{2+} etc.) and M^{2+} an ionised cation, i.e. one which has lost another electron (Na^{2+}, K^{2+}, Sr^{3+}, Ba^{3+}, etc.). [See, however, the scheme on p.68, reaction (2c). (Ed.of Translation)].

The mechanism of the radiolysis of alkali metal nitrates examined above can probably be extended to the nitrates of alkaline earth metals. In the nitrates of heavy metals or variable-valence metals quite different electronic-ionic processes occur, whose importance is evident from the examination of the effect of impurities on the radiolysis of the nitrates[8,19,24,39].

III. RADIOLYSIS OF NITRITES

Alkali metal nitrites are extremely stable under the action of radiation[41]. The only products observed on irradiation of sodium nitrite are the paramagnetic species NO_2 and $N_2O_4^-$.[41-44] The signal detected after irradiation at 77°K (a strongly anisotropic triplet) has been attributed[42,43,45] to NO_2 molecules located in the *bc* plane of the crystal. These species disappear on heating the crystals to room temperature.

However, sodium nitrite irradiated at 20°C at doses of about 100 Mrad also gives a distinct ESR signal consisting of an anisotropic triplet on which a quintet is superimposed. It has been shown[41-44] that the first signal originates from NO_2 molecules in the *ac* plane of the crystal and the second is due to $N_2O_4^-$ ions formed as a result of the transition of NO_2^- ions or more probably NO_2 molecules into neighbouring cationic vacancies with rotation by 180° and formation of an N–N bond between these species and neighbouring normal anions. Optical absorption spectra in the visible and in the infrared regions[45-47] confirm this view.

IV. RADIOLYSIS OF CHLORATES, BROMATES, AND IODATES

1. ESR and Optical Spectra of Irradiated Salts

At the present time ESR spectra have been investigated in relatively high detail only for potassium and sodium chlorates irradiated with comparatively low doses ($< 10^6$ rad). The data concerning the signals from caesium and rubidium chlorates are extremely limited, while for bromates and iodates there is only a general indication of the possibility of detecting signals due to paramagnetic species in these salts and a brief description of the form of such signals in the spectra of powdered materials[48].

The ESR spectra of irradiated alkali metal chlorates are complex (Figs. 5 and 6). There exist different views in the literature concerning the interpretation of each signal in the spectrum (see Table 6). In later studies on the ESR spectra of irradiated sodium chlorate[49,54-56] it has been shown that at irradiation doses up to about 10^5 roengtens three paramagnetic centres are evident, their number increasing on further irradiation. The attention of the investigators has been drawn most to the complex signal, observed in almost all the studies, consisting of four anisotropic quartets.

Some workers[51,53,54] attribute this signal to the $ClO-ClO_3^-$ group, while Gamble[49] assigned it to ClO_3 radicals. The analysis of the signal in the latter study[49] shows, however, that its parameters (hyperfine structure and *g*-factor) differ appreciably from those of the spectra of ClO_3 captured in various matrices[50] and therefore the models of this centre proposed by Hasty[51] and Ramasastry et al.[52] must be preferred (see Figs. 5 and 6).

Studies of the ESR spectra at low temperatures (irradiation of crystals with fast electrons and recording of the spectra at 77°K) led to a new spectrum[50], which can be more definitely assigned to ClO_3 (Fig. 6). This radical proved to be extremely unstable; it breaks down on storage and under the action of light at 77°K after 35 and 15 min respectively.

The distinct central singlet in the spectra of irradiated chlorates has been attributed[52-54] to O_3^-. Probably this interpretation is correct, although it has been suggested[51,57,58] that the signal is due to the radical-ion O_2^-.

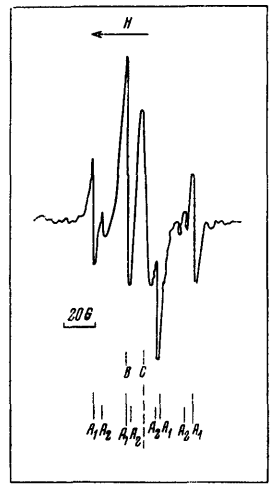


Figure 5. ESR spectrum of irradiated sodium chlorate (specimen irradiated and spectrum recorded at room temperature)[49]; A_1 and A_2–quartets due to splitting by ^{35}Cl and ^{37}Cl nuclei; *B* and *C*–singlets.

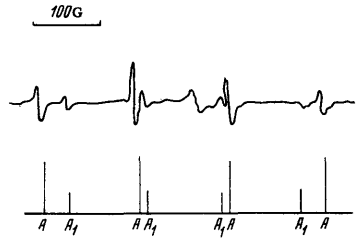


Figure 6. ESR spectrum of irradiated sodium chlorate (specimen irradiated and spectrum recorded at 77°K)[50]; A_1 and *A* as in Fig.5.

Table 6. *g*-Factors of the ESR signals from irradiated chlorates.

Radical				References
$O_3^-(O_2^-)$	ClO_3	ClO	ClO_3 / $ClO-ClO_3^-$	
g=2.00				51
g=2.0095	g=2.01	g=2.022 (position of the most intense line)	g=2.0023	52
	g=2.0102			53
			g=2.0085–2.009	49
g=2.0338			g=2.0124	54
	g=2.0033		2.003	55
	g=2.0032		2.0026	56
			g=2.0107–2.0135	50

The characteristic doublet observed in a number of studies has been assigned by all the investigators to ClO_2, the remaining lines of the ESR spectrum of this radical (it gives rise to a quartet) being masked by other signals which are in no way related to it. However, it should be noted that the parameters of this signal attributed to ClO_2 by Fayet and Thieblemont [55] differ from those found by Ramasastry et al. [52]

Apart from the identification of different species enumerated above, a number of investigators have observed in the spectra of chlorates irradiated at room temperature lines due to various unidentified centres [49,52,55]. The results obtained by Subbotin [54] show that the ESR spectra of the powdered salts irradiated at room temperature are qualitatively similar for all the alkali metal and alkaline earth metal chlorates. Data on the accumulation kinetics and the behaviour of the signals from a number of chlorates after annealing and on the relation between the rate of accumulation and the crystal lattice parameters were obtained for the first time [48,50] from the ESR spectra of alkali metal chlorates, the specimens being irradiated and the spectra recorded at 123° and 77°K. The irradiation of the salts at low temperatures with high doses (up to 10^8 rad) made it possible to obtain for the first time signals from bromates and iodates and to observe signals from potassium chlorate not detected previously. Nuclear quadrupole resonance signals due to ^{35}Cl nuclei in potassium and sodium chlorates have been described in certain brief communications [59-61]. The deformation of the lattices of these salts in the vicinity of the radiolysis products leads to the appearance of broad signals which have not been interpreted hitherto.

The information about the absorption spectra of irradiated salt layers of the type MXO_3 (X = halogen) are also extremely limited. Heal, who investigated the absorption spectra of thin single-crystal potassium chlorate plates irradiated with X-rays up to high doses (10^{23} eV g^{-1}), [62] established the presence in the spectra of three absorption bands—at 260 nm, 310 nm, and in the region of about 450 nm. By analogy with the positions of the absorption bands of oxychlorine anions in aqueous solutions (cf. Ref. 63), he attributed these bands respectively to ClO_2^-, ClO^-, and Cl_2O_6 and confirmed their presence by analysing the solution of the irradiated salt. In contrast to Heal's data, other investigators [52,64-66] observed only one band in the spectrum of irradiated potassium chlorate, with a maximum at 461 nm, which is stable at room temperature. When crystals irradiated with X-rays are exposed to light, an additional band appears at 340 nm (and at the same time also a new signal in the ESR spectrum), which has been attributed [65] to Cl_2^-. Under the same conditions, two absorption peaks, displaced towards the short-wavelength region of the spectrum, have been observed [64] in the spectrum of sodium chlorate.

A more detailed study of the colouring of sodium and potassium chlorates at room temperature [67,68] showed that in the spectrum of irradiated sodium chlorate there are three absorption regions: at wavelengths less than 260 nm and with maxima at 302–310 and 420 nm. The observed spectrum is believed [68] to consist of individual bands with maxima at 228, 260, 310, 360, and 420 nm for sodium chlorate and at 216, 260, 310, 360, and 450 nm for potassium chlorate. It is reasonable to assign the absorption at 260, 310, and 360 nm to ClO_2^-, ClO^-, and ClO_2 respectively. It is believed [68] that the absorption band at 216–220 nm is due to the transition of an electron from ClO_3^- to a lattice defect (analogue of the α-band in alkali metal chloride crystals), and the absorption in the region 420–450 nm is attributed to Cl_2O_6 and O_3^- or to simultaneous absorption by these species. The nature of the thermal and optical bleaching of the absorption bands studied in the same investigations [67,68] confirmed the hypothesis put forward concerning the structure of the absorption centres [67].

The models of the centres (enumerated above) responsible for the optical absorption in irradiated chlorates are the most likely. Apart from those described, there are, however, other hypotheses about the structure of the absorption centres [51,54].

2. Composition of Stable Radiolysis Products

In the first studies on the radiolysis of chlorates [64,68] the presence of oxygen, Cl^-, and ClO_2^- in the products was established. The composition of the radiolysis products was investigated in detail by Heal [62]. By analysing the solutions of irradiated potassium chloride and by absorption spectroscopy of the crystals, he determined the following stable products: O_2, Cl^-, ClO^-, ClO_2^-, ClO_4^-, and small amounts of Cl_2O_6 and ClO_2.

The initial radiochemical yields G_0 of the main radiolysis products of alkali metal chlorates and bromates based on the work of a number of investigators [69-77] are compiled in Table 7. Fig. 7 shows the accumulation curves for the radiolysis products of potassium chlorate [62].

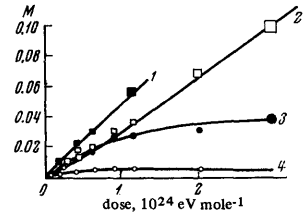


Figure 7. Accumulation curves for the main radiolysis products in potassium chlorate at room temperature [62]:
1) O_2; *2*) Cl^-; *3*) ClO_2^-; *4*) ClO^-.

Studies on the radiation chemistry of bromates [70-75] established that their irradiation in a nuclear reactor with mixed radiation (γ-rays, fast and slow neutrons) and with cobalt-60 γ-rays leads to the accumulation of the radiolysis products Br^-, Br_2, BrO^-, and BrO_2^-, i.e. the composition of the reduction products of bromate ions is similar to that of the products found in the radiolysis of chlorates. The products also contain O_2, but the presence of BrO_4^- has not been finally established. Chase and Boyd [78] also detected BrO^-, BrO_2^-, Br^-, O_2, and BrO_2 (the last tentatively) in aqueous solutions of alkaline earth metal bromates.

3. Kinetics of Radiolysis

A constant rate of accumulation of Cl^- and O_2 and a complex shape of ClO_2^- and ClO^- accumulation curves are characteristic of chlorates. Characteristic features of potassium chlorate, which has been investigated in greater detail, are also the insignificant effect of temperature in the range 77–300°K on $G(-ClO_3^-)$ and the probable formation of appreciable amounts of ClO_4^- or Cl_2O_6.

A group of studies on the Szillard–Chalmers effect in this class of compounds[79-81] is related to the investigations of the radiolysis of chlorates. Among the products in chlorates irradiated with neutrons, Cl^-, ClO_2^-, ClO^-, Cl_2, and ClO_4^- have been noted.

The radiolysis of alkali metal bromates has been investigated in greatest detail by Boyd and coworkers[72-75,82] (Table 7). The accumulation of Br^- is linear in the initial stage of the radiolysis (approximately up to 1×10^{23} eV g^{-1}); then it begins to take place with a gradually decreasing rate for all the bromates, except lithium bromate, the degree of deviation from linearity increasing in the series from lithium bromate to caesium bromate. In the temperature range 77–358°K the rate of radiolysis depends only very slightly on the irradiation temperature. The rate of accumulation of Br^- in caesium bromate is almost independent also of the irradiation dose rate.

One of the principal conclusions arrived at by Boyd et al.[72] is the correlation which they established between the "free space" in bromates and radiation stability. Such correlation holds also for a number of other inorganic salts[38].

Table 7. The yields of the main radiolysis products of salts of the type $MHalO_3$.

Irradiated compound	Products					References	Remarks
	G (Hal^-)	G ($HalO^-$)	G ($HalO_2^-$)	G (O_2)	G ($-HalO_3^-$)		
$NaClO_3$	2.14	—	—	—	—	76	α-Particles
$KClO_3$	0.4	—	1.2	1.57	—	64, 69	Room temperature, X-rays
$LiBrO_3$	0.13	0.21		—	0.23	72	Room temperature
$NaBrO_3$	0.88	0.64		—	1.48		
$KBrO_3$	1.07	0.46		—	1.53		^{60}Co γ-rays
$RbBrO_3$	1.02	0.82		—	1.85		
$CsBrO_3$	2.23	0.49		—	2.73		
Li^7BrO_3	—	—	—	—	0.47	74	Room temperature
$NaBrO_3$	0.59	0.22	0.59	—	1.4		Mixed reactor radiation
$KBrO_3$	0.63	0.20	0.54	—	1.3		
$RbBrO_3$	0.96	2.23	0.31	—	2.4		
$CsBrO_3$	0.61	—	—	—	3.4		
$LiBrO_3$	0.58	0.26	0.47	—	1.4		

Boyd[73] established that certain kinetic parameters of the radiolysis of lithium bromate under the action of neutrons differ from those which they described for γ-irradiation. In particular, the radiation yields are much higher (Table 7). For all the other bromates, the yields of products on γ-irradiation and irradiation in a reactor are very similar. The higher yield for lithium bromate is associated with the high efficiency of neutron capture by ^6Li nuclei. Thus, when mixed reactor radiation is used, the isotope composition influences the rate of radiolysis.

Among alkali metal bromates, the radiolysis of caesium bromate has been investigated in greatest detail[75]. Some information about the kinetics of product accumulation in the radiolysis of alkaline earth metal bromates has been published by Chase and Boyd[78] who noted a change in the yields with dose for all the products resulting from the secondary reactions involved in the thermolysis and annealing of the radiolysis products.

4. Mechanism of Radiolysis

The above data provide a basis for a mechanism of the radiation-induced decomposition of alkali metal chlorates. The following fundamental reactions are likely to occur in the radiolysis of the chlorates:

1. $ClO_3^- \xrightarrow{h\nu} ClO_3^{-*}$ → $ClO^- + O_2$, (a); → $ClO_2^- + O$, (b); → $Cl^- + {}^3/_2O_2$, (c); → $ClO + O_2^-$, (d); → $ClO_2 + O^-$, (e)
2. $ClO_3^- \xrightarrow{h\nu} ClO_3 + \bar{e}^*$, (a)
   $M^+ \xrightarrow{h\nu} M^{2+} + \bar{e}^*$, (b)
   $M^{2+} + ClO_3^- \rightarrow M^{3+*} + ClO_3^*$, (c)
3. $\bar{e}^* \rightarrow \bar{e}$, → $ClO_2 + O$, (a)
4. ClO_3^*, ClO_3 → $ClO + O_2$, → $Cl + O_2 + O$, (b)
5. $ClO_3 + e \rightarrow$ products 1a–1e (a)
   $ClO + ClO_3^- \rightarrow (ClO{-}ClO_3^-)$, (b)
6. $O_2^- + O \rightarrow O_3^-$, (a)
   $O_2 | \square a + \bar{e} \rightarrow O_2^- | \square a$, (b)
7. $O + O \rightarrow O_2$, (a)
   $Cl + Cl \rightarrow Cl_2$, (b)
8. $ClO_2^- \rightarrow Cl^- + O_2$, (a)
   $ClO^- \rightarrow Cl^- + O$, (b)
9. $ClO_2^- + O \rightarrow ClO_3^-$, (a)
   $ClO^- + O \rightarrow ClO_2^-$, (b)
10. $ClO_3^- + O \rightarrow ClO_4^-$, (a)
11. $ClO_3 + ClO_3 \rightarrow Cl_2O_6$, (a)
    $Cl_2O_6 + e \rightarrow ClO_3^- + ClO_3$. (b)

In the primary stage both excitation [reaction (1)] and ionisation [reaction (2)] of anions take place. The dissociation of excited ClO_3^{-*} species can result in the formation of various oxychlorine products [reactions (1a)–(1e)]. However, the formation of oxychlorine anions [reactions (1a)–(1c)] is more likely than reactions (1d) and (1e) because of the higher electron affinity of chlorine oxides compared with oxygen[40].

The following experimental findings confirm the occurrence of ionisation in chlorates: (1) the presence at low temperatures in irradiated sodium and potassium chlorates of a signal originating most probably from ClO_3;[50] (2) the formation on radiolysis of small amounts of Cl_2O_6 [76] produced as a result of bimolecular interaction between ClO_3 species [stage (11a)]. After the ionisation step, the excited electron loses its energy [the electron thermalisation stage, reaction (3)], and is then captured by a trap.

Reactions (2b) and (2c), the ionisation of the cation and subsequent conversion into M^{2+*} under the influence of the powerful field of the electron in the neighbouring anion, probably also occur. The excited radical ClO_3^* produced at the same time breaks down; among its possible decomposition products, only ClO_2 radicals have been observed so far.

In view of the high electron affinity of ClO_3 ($E = 3.96$ eV according to Ref. 40), the recombination of these species

[reaction (5)] can also lead to bond dissociation within the radical. The possibility of this occurring is largely determined by the ratio of the electron affinity of ClO_3 to the dissociation energy of Cl–O bonds in the chlorate. The latter is 2.38 eV in potassium chlorate [11]. The adoption of the $ClO–ClO_3^-$ pair as one of the paramagnetic centres in chlorates presupposes reaction (5b).

In the ESR spectra of irradiated chlorates one of the singlets has been assigned to the oxygen radical, which justifies the introduction of reaction (6a), but according to the latest studies stage (6b) is the more likely.

By analogy with bromates, one may assume that the annealing of the radiolysis products which occurs also in the radiolysis process itself at moderate and high temperatures involves both thermal conversion of unstable products [reactions (8a) and (8b)] and the reverse oxidation of oxychlorine products by atomic oxygen [reactions (9a) and (9b)] formed on decomposition of excited species [reactions (1), (4), and (5)].

It is at present difficult to determine the subsequent fate of the ClO_3 radicals formed in stage (2) (decomposition or dissociative recombination with an electron). However, the first data obtained on the thermal and optical bleaching of ClO_3 at low temperatures [50] suggest that reaction (5) is the more likely process, although reaction (11a) and the subsequent reaction (11b) are possible.

In view of what has been said, one might think that neutral oxychlorine radicals (ClO, ClO_2) and anions (ClO^-, ClO_2^-) are formed in chlorates by different reactions [reactions (2) and (4) and reactions (1) and (5) respectively]. Since the presence of the ClO_4^- anions in the radiolysis products of chlorates has been demonstrated in a number of studies and Sharman and McCallum [80] assert that ClO_4^- anions are formed by the further oxidation of chlorine in the chlorate anion, one must introduce tentatively reaction (10).

The formation of radicals and final products in the radiolysis of alkali metal bromates has been investigated in much less detail than for the chlorates. Only the problem of the accumulation of bromide and oxybromine anions with a low degree of oxidation of bromine has been adequately dealt with in the literature. The mechanism put forward [73,74] for the radiolysis of bromates appears to be less definite and justified than the set of fundamental stages which can be postulated for chlorates. It may be supposed (the comparison of the compositions of the molecular radiolysis products of chlorates and bromates confirms this) that the mechanism of the radiolysis of $MBrO_3$ is largely similar to that of the radiolysis of chlorates. The differences in the mechanism of radiolysis of these two groups of salts can be definitely established only by a thorough comparative study of the optical and ESR spectra of the salts.

V. RADIOLYSIS OF PERCHLORATES

The radical products of the radiolysis of potassium and ammonium perchlorates have been determined and investigated by the ESR method by a number of workers [83–90]. The presence of the paramagnetic species ClO_2 and O_3^- in potassium perchlorate irradiated at room temperature has been established [3,84] and certain kinetic characteristics of their accumulation and thermal breakdown have been determined [83]. By irradiating the specimens and recording the spectra at low temperatures, it is possible to observe two additional signals, one of which has been attributed [83] to O_3^-, while the other has remained uninterpreted. A study in the temperature range 77–100°K revealed two further ESR signals, which have been assigned tentatively to ClO_4 radicals [90].

The relatively stable ClO_3 and NH_3^+ species have been observed and definitely identified in irradiated ammonium perchlorate, while Boyarchuk et al. [85] also observed at low temperatures an unstable singlet which they attributed to electrons localised at lattice defects.

Among all the radicals enumerated, only the behaviour of NH_3^+ in ammonium perchlorate has been investigated in fair detail. The spectroscopic and kinetic characteristics of other paramagnetic centres have not been studied, nor have the ESR spectra of any other perchlorates. Optical absorption by radiolysis products in solid perchlorates has been investigated only for ammonium perchlorate [63,91]. Absorption bands with maxima close to 260, 300, and 360 nm, indistinct absorption near 420 nm, and absorption at wavelengths below 220 nm have been detected in the spectrum of ammonium perchlorate irradiated at 77° and 300°K. Comparison with the spectra of irradiated chlorates, aqueous solutions of the corresponding compounds, and the results of the analysis of the stable products of the radiolysis of ammonium perchlorate, led the authors to assign these bands to ClO_2^-, ClO^-, ClO_2, O_3^- (Cl_2O_6), and Cl_2^- respectively.

Heal [92] identified Cl^-, ClO_3^-, and O_2 as the stable radiolysis products of potassium perchlorate, after dissolving the irradiated salt in water. However, Baberkin et al. [69] have stated that the chloride appears only after heating the irradiated specimens above 370°K. Heal [92] has suggested the formation of hypochlorite and chlorite ions, whose presence in irradiated alkali metal and alkaline earth metal perchlorates was demonstrated later [93–96]—these studies showed that ClO_2 and metal oxides are also formed. The variation of the degree of accumulation of the main radiolysis products with the dose absorbed differs little from linearity. The deviations from linearity at high irradiation doses are due to secondary reactions involving the annealing and thermolysis of the products. The radiochemical yields of the radiolysis products of various metal perchlorates are listed in Table 8, which shows that the main radiolysis products of the perchlorates are chlorate and oxygen. The remaining products are formed with relatively low yields. It has been shown [93–95] that $G(-ClO_4^-)$ for potassium and sodium perchlorates is almost independent of temperature over a wide range of the latter.

Table 8. Radiochemical yields of the radiolysis products of perchlorates at room temperature.

Salt	$G(ClO_3^-)$	$G(ClO_2^-)$	$G(ClO_2)$	$G(ClO^-)$	$G(Cl^-)$	$G(O_2)$	$G(-ClO_4^-)$	References
$LiClO_4$	2.80	0.15	0.59	0.10	0.12	2.15	3.76	94
$NaClO_4$	3.57	0.17	0.11	0.09	0.42	2.96	4.36	94
$NaClO_4$	2.8	0.75	0.08	0.1	0.43	—	4.2	93
$KClO_4$	2.99	0.18	0.12	0.09	0.45	2.68	3.83	94
$KClO_4$	—	—	—	—	0.94	—	3.46	96
$RbClO_4$	4.06	0.20	0.12	0.14	0.75	3.84	5.27	94
$RbClO_4$	—	—	—	—	1.14	—	4.86	96
$CsClO_4$	5.28	0.22	0.10	0.17	1.07	5.28	6.84	94
$CsClO_4$	—	—	—	—	1.94	—	8.84	96
$Mg(ClO_4)_2$	4.29	0.14	0.07	0.03	0.15	2.62	4.67	94
$Ca(ClO_4)_2$	3.44	0.00	0.51	0.08	0.12	1.99	4.15	94
$Sr(ClO_4)_2$	3.90	0.19	0.14	0.11	0.19	2.61	4.58	94
$Ba(ClO_4)_2$	1.76	0.84	0.42	0.12	0.06	2.18	3.20	94

The relative content and the kinetics of the accumulation of stable radiolysis products, observed after dissolving irradiated ammonium perchlorate in water, differ from those quoted for alkali metal perchlorates. It has been shown[63,91,97,98] that the main radiolysis products are Cl^-, ClO_3^-, and Cl_2; the question of the presence of ClO_2^- and ClO^- in aqueous solutions of irradiated ammonium perchlorate remains open (see Table 9).

The accumulation of products is non-linear because of the thermolysis during irradiation (even at room temperature) of oxychlorine radiolysis products, but the overall yield $G(-ClO_4^-)$ in the radiolysis process remains constant. Attention has been drawn to the effect of LET on the yields of the radiolysis products[63,91].

The composition of the gaseous radiolysis products was established mass-spectrometrically only for ammonium perchlorate[63,99]. In irradiated crystals O_2, HCl, and N_2O retained by the lattice have been observed[99]—N_2O, NO, O_2, and H_2O are evolved from the crystals during radiolysis[63].

Table 9. Initial yields of the radiolysis products of ammonium perchlorate at room temperature.

Type of radiation	$G(ClO_3^-)$	$G(ClO^-+Cl_2)$	$G(Cl^-)$	$G(-ClO_4^-)$	References
200 kV X-rays	1.78±0.15	0.78±0.1	2.1±0.1	4.36±0.15	63
4.7 MeV protons	1. 8±0.1	1. 8±0.1	2.7	6. 8±0.15	91
^{60}Co γ-rays	1. 3	1.65	2.5	—	98

The post-radiative changes in the properties (mainly thermal stability) of ammonium perchlorate have been examined in a number of studies[100-105]. Stable final radiolysis products which catalyse thermal decomposition must probably be regarded as responsible for the increased rate of thermolysis of irradiated ammonium perchlorate. The data available at the present time on the composition and properties of intermediate and to some extent final radiolysis products are insufficient for the construction of soundly based mechanisms for the radiolysis of perchlorates at various temperatures. Therefore the mechanisms proposed for the individual intermediate stages of the radiolysis of perchlorates[63,83,91,94-96,106] must be regarded as tentative.

The principal postulates put forward in the construction of these mechanisms are as follows. It is suggested that the primary radiolysis products are mainly Cl^-, O_2, and ClO_3^-. The predominant formation of ClO_3^- as the primary product in the radiolysis of ammonium perchlorate has been pointed out[63,91]. Data on the effect of semiconductor impurities on the radiolysis of ammonium perchlorate[63,107,108] suggest that the products are formed on dissociative addition of an electron to ClO_3 and ClO_4 radicals. The important role of the interaction between the radiation and the cation, which leads to the formation of species with two and more positive charges, has been pointed out[106].

VI. ANNEALING AND INTERCONVERSIONS OF RADIATION-DAMAGED REGIONS

A number of investigators have undertaken, particularly in recent years, the study of processes involved in the restoration of the properties and the stoichiometric composition of irradiated materials, under the influence of various factors on the irradiated compounds. Frequently in studies of this kind thermolysis and interconversions of the radiolysis products are observed together with the intrinsic annealing. Studies in this field consist of two groups in each of which the problem is formulated in a slightly different way.

Most of the investigations deal with the study of the annealing phenomena in preparations (mainly inorganic oxygen-containing salts stable to radiation) irradiated with slow neutrons. Problems concerning isotope separation using the Szillard–Chalmers effect and the time-variation of isotope distribution between the individual chemical species in irradiated materials have been mainly examined (for reviews, see Refs. 109–111).

A comparatively small number of publications concern the changes in the concentrations of the radiolysis products in solid salts during post-radiative annealing. Most of these studies have been carried out on potassium nitrate and certain heavy metal nitrates. The available literature data are concerned almost exclusively with the kinetics of thermal annealing[10,14,15,38,94,112-118], while the post-radiative changes in the products under the influence of other factors have been investigated very little.

Annealing in nitrates is regarded approximately as the oxidation of nitrogen–oxygen products (mainly NO_2^-) by radiolytic oxygen[112,113]. The rate and extent of this process are significantly influenced by all types of treatment of the salt: pressing[113,114,116], grinding[115], introduction of heterovalent ions into the lattice[39]. Annealing is greatly accelerated at the polymorphic transition temperatures[117]; in some nitrates it appears to involve a more complex mechanism than simple oxidation of NO_2^- by oxygen trapped in the lattice. There must be various mechanisms of the effects of the preliminary treatment on thermal annealing[114,115].

Among cases of non-thermal annealing, a decrease of the amount of radiolytic NO_2^- in lead nitrate on pressing[114] and irradiating the preparation with ultraviolet light has been observed.

Unstable radiolysis products of oxyhalogen salts can also undergo changes during annealing of the irradiated compounds[72,75,76,94,119-121]. According to some investigators[72,75,111,121-123], two groups of reactions then occur–recombination of oxychlorine or oxybromine products with oxygen (i.e. the intrinsic annealing) and their thermolysis to the chlorides. In alkali metal and alkaline earth metal bromates these reactions take place during the irradiation process itself even at room temperature and result in variable yields of the products during radiolysis.

VII. RELATIVE STABILITY TO RADIATION IN SERIES OF SIMILAR SALTS

It has now been firmly established that the stability of inorganic compounds (including oxygen-containing salts) to radiation is determined both by their macroproperties, in particular the structural and energy properties[94-96], and the nature and type of damage to the crystal lattice[107,124].

One of the most clearly established relations between stability and macroproperties of similar salts is that, on substitution of the cation in series of salts with the same anion, the radiation yield of the products changes smoothly and in parallel with the variation of the most important characteristics of the crystal lattice ("free space" and lattice energy, electronic fraction of the ions, etc.). The study of relations obtaining in radiolysis in series of similar compounds over a wide range of temperatures[48,50,125]

and in the annealing of nitrates [118] and also the study of the radiolysis of aqueous perchlorate systems [106] permit a more detailed examination of this problem. In particular, three temperature regions may be isolated in which the origins of stability series and the very nature of the relations obtaining in series of compounds may be different.

At low temperatures (77°K) the accumulation in alkali metal bromates and chlorates of radical products of the ionisation of anions takes place with a yield which increases in the series in parallel with the increase of the electronic fraction of the anion [50]. At the same time other radicals, whose yield increases in the opposite sense, i.e. in parallel with the increasing electronic fraction of the cation and the "free space" in the lattice, become stabilised under these conditions.

At higher temperatures (between 120° and 150°K) the radicals of the first type disappear, while the yields of those of the second type increase. Probably, starting with the above temperatures, the overall rate of accumulation of products in series of compounds with a variable cation or anion (for example, in the second case in the series $KClO_3$–$KBrO_3$–KIO_3) increases in parallel with increasing "free space" and electronic fraction of the cation. A similar relation is also observed in the accumulation of final, molecular radiolysis products, which are analysed chemically.

Similar relations (as regards stable products) have been established by a number of workers for alkali metal and (in a number of cases) alkaline earth metal halides, azides, nitrates, chlorates, bromates, perchlorates, and permanganates [38,50,78,106,126] and they are probably common to inorganic salts irradiated close to room temperature. Until recently it has been assumed that the direct origin of series relations of this type is associated with the change only in the *"free space" of the crystals* in the series of salts. As the "free space" increases, the cage effect and the probability of the reverse reactions of the intermediate radiolysis products decrease, which in fact entails an increase of the radiation yields of the products.

However, recently it has been suggested that the change in "free space" cannot be regarded as the only origin of related series in the temperature range investigated. According to some investigators [3,4,93,106], the interaction between radiation and the salt cations must make a significant contribution to the yields of the radiolysis products. This view was confirmed experimentally for the first time for silver nitrate and alkali metal perchlorates by Mosley and Moulton [12] and Wang Wen-hsin et al. [106] respectively. The interaction between radiation and cations which takes place with a probability proportional to the electronic fraction of the latter leads to the formation of additionally ionised cations (mainly M^{2+}), whose coulombic field may be sufficient to remove an electron from a neighbouring anion [106]. The energy evolved on addition of an electron to M^{2+} may result in the decomposition of neighbouring radicals and anions.

Finally, in radiolysis at elevated temperatures (different for different salts) it is desirable to take into account the effect of annealing processes, occurring during irradiation, on the yields of products and the occurrence under these conditions of radiation stability series. According to Zakharov et al. [118], the rate and extent of annealing in alkali metal nitrates increase appreciably in the series ranging from sodium nitrate to caesium nitrate, which means that they vary in parallel with the increase of "free space", i.e. with the improved conditions for the diffusion of radiolysis products. The activation energy for the annealing in nitrates is much higher than the activation energies for the processes occurring in radiolysis. Therefore the variation of radiation stability in series of these salts at elevated temperatures must be less pronounced and possibly (if not prevented by thermolysis) actually the reverse of the variation of radiation stability at low temperatures [118].

The rates of annealing (re-oxidation) and thermolysis of the oxyhalogen products in perchlorates, chlorates, and bromates also depend on the "free space" [78,94]. This must affect the radiation stability series for the salts at elevated temperatures.

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Tomsk Polytechnic Institute

Autocatalytic and Impedance Phenomena and the Effect of the Physical State of the Solid Product on the Acceleration and Retardation of Reversible Topochemical Reactions with Participation of Solid and Gaseous Reactants

E.S.Vorontsov

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I. INTRODUCTION

During the last 2–3 decades significant advances have been made in the chemistry of solids [1–16]. However, it is noteworthy that many problems of the kinetics and mechanism of heterogeneous reactions involving solids are only in the initial stage of development. Furthermore, the development and research in this field and the accumulation of experimental data make it necessary to revise or correct the classical hypotheses in this branch of science.

The present review deals with the most important kinetic features of reactions of the type

$$A(solid) + C(gas) \rightleftarrows B(solid), \quad (1)$$

$$A(solid) + C(gas) \rightleftarrows B(solid) + D(gas). \quad (2)$$

Reactions of the first type include the formation of metal oxides, sulphides, selenides, and halides, the hydration of oxides and their conversion into carbides, and the reverse reactions. Processes of the second type include numerous reactions involving the reduction of oxides to the metals by gaseous reducing agents and the reverse reactions, as well as certain other interactions. Reactions (1) and (2) are heterogeneous and take place at an interface. Therefore the physical state and the topography of the surface of the initial solid phase A and the product B play a very important role in the kinetics of these processes.

The intrinsic chemical step is complicated by a number of physical phenomena which accompany it: the rearrangement of the crystal lattices of the interacting phases and their recrystallisation and sintering, the diffusion of the reactant C and the product B in the gaseous medium and their motion through pores and cracks in the solid phases A and B, the adsorption and desorption of gases, and the supply and removal of heat. Therefore the processes can take place both under kinetic and diffusion-dependent conditions.

In the examination of the kinetics of reactions (1) and (2) under isothermal conditions (this is the case most frequently encountered in technology), we shall distinguish two factors which have been called "autocatalysis" and "impedance".

Autocatalysis consists in the reaction, having begun after a certain induction period, developing at an increasing rate, the process gradually coming to a stop only at more advanced stages as a result of the disappearance of the initial reactant. The accumulation of the product of an autocatalytic reaction can be described graphically by an S-shaped curve and mathematically the relation between the extent of reaction α and time t can be expressed by the Kolmogorov–Erofeev equation, for example [17]:

$$\alpha = 1 - \exp(-kt^n). \quad (3)$$

The self-acceleration of the reaction and a rate maximum on the kinetic curve have been observed experimentally in numerous investigations [18–27].

Another no less interesting feature of reactions (1) and (2) is that the formation of the product B results in the separation of the reactants in space and the appearance of factors hindering the process, whose magnitude increases as the solid product accumulates. This phenomenon has been called impedance. Factors hindering the reaction can arise even at the very beginning, whereupon the rate will steadily decrease (provided, of course, that there are no abrupt changes in the nature of the process itself, the